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(71) Applicant
Allied Corporation (USA–New York),
Columbia Road and Park Avenue, Morris Township, Morris County, New Jersey 07960, United States of America

(72) Inventors
Paul Robert Gifford
James Barry Palmisano

(74) Agent and/or Address for Service
J A Kemp & Co,
14 South Square, Gray's Inn, London WC1R 5EU

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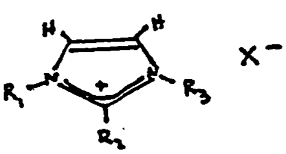
H1B

(54) **Room-temperature molten non-aqueous electrolyte**

(57) A molten, non-aqueous electrolyte composition containing admixtures of aluminium halide and 1,2,3-trialkylimidazolium halides having the formula TimX:



wherein R_1, R_2 and R_3 are independently alkyl groups of 1 to 12 carbons especially linear alkyl groups of 1 to 5 carbons and X is halide or mixtures of halides, e.g., bromide and/or chloride is disclosed. The electrolyte composition may also contain an electrochemically-inert organic liquid, e.g., benzene or acetonitrile and/or alkali metal (especially Li^+) and/or tetraalkylammonium salt. The molar ratio of aluminium (denoted by Al) to trialkylimidazolium (denoted by Tim) may be varied over a wide range so as to make the molten electrolyte composition basic, neutral or acidic and as such the electrolyte is useful in batteries, especially secondary batteries.

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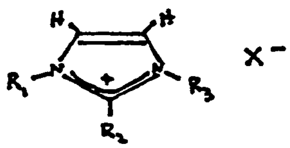
SPECIFICATION

Room-temperature molten non-aqueous electrolyte

BACKGROUND OF THE INVENTION

This invention relates to a molten, non-aqueous electrolyte containing admixtures of aluminium halide and 1,2,3-trialkylimidazolium halides have the formula TimX:



wherein R_1, R_2 and R_3 are independently alkyl groups of 1 to 12 carbons and X is halide, e.g., bromide and/or chloride. The molar ratio of aluminium (denoted by Al) to trialkylimidazolium (denoted by TimX) may be varied over a wide range so as to make the molten electrolyte composition basic, neutral or acidic and as such the electrolyte is useful in batteries, especially secondary batteries.

The use of mixtures of 2 moles of anhydrous aluminium halide such as $AlCl_3$ and 1 mole of a N-alkylpyridinium bromide or chloride as a liquid electrolyte for electrodepostion of aluminium on a metal cathode such as iron at about room temperature is disclosed in U.S. Patent Nos. 2,446,349 and 2,446,350. Also see U.S. Patent No. 2,446,331. U.S. Patent No. 4,115,390 (J. Nardi) and U.S. patent No. 4,122,245 (J. Nardi, et al.) described the preparation of 1-alkylpyridinium chloride salts and the use of these salts for the preparation of 2:1 (mole/mole) $AlCl_3$: 1-alkylpyridinium chloride room-temperature molten salt electrolytes. U.S. Patent No. 4,122,245 discloses that the 1-alkylpyridinium molten salts are useful as ambient temperature battery electrolytes and describes a test cell employing aluminium or glassy carbon as the anode and chloranil as the cathode.

U.S. Patent No. 4,355,086 (Saathoff et al.) discloses that the discharge rate and internal conductivity of a lithium thionyl chloride battery is improved by the addition of a mixture of aluminium chloride and n-butylpyridinium chloride to the cell electrolyte.

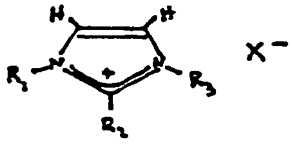
The preparation and use of 1,3-dialkylimidazolium chloride salts with aluminium chloride for room-temperature molten salt electrolytes in a battery cell having an aluminium anode and a iron(III)chloride cathode is described by J.S. Wilkes, et. al. in the Frank J. Seiler Research Laboratory Technical Report FJSRL-TR-81-0011; ADA 107,989, October, 1981 and Inorg. Chem. 1982, 21, 1263–1264. Wilkes et al. assert that the 1,3-dialkylimidazolium chloroaluminate melts provide an increased liquidus composition range and improved stability to electrochemical reduction compared to the 1-alkylpyridinium chloride-based melts.

R.A. Osteryoung and coworkers at SUNY at Buffalo (J. Electrochem. Soc. (1983), 130 (No. 9) at pages 1965-1967 and 1968–1969) suggest that neutral room-temperature molten salts such as alkylpyridinium chloride or 1,3-dialkylimidazolium chloride-aluminium chloride might be useful for studies of polymer electrodes.

There is still a need for a room-temperature, molten non-aqueous ionic liquid electrolyte having various physical and chemical properties superior to those of previously reported molten ionic liquid electrolytes, and especially having superior stability to electrochemical oxidation and reduction over a wider liquid composition range.

SUMMARY OF THE INVENTION

The present invention provides a molten non-aqueous electrolyte composition comprising an admixture of aluminium halide, AlX_3 and a 1,2,3-trialkylimidazolium halide having the formula, TimX:

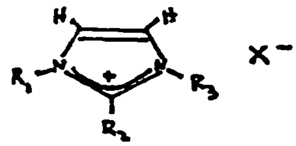


wherein R_1, R_2 and R_3 are independently alkyl of 1 to 12 carbons and X is independently halide or mixtures of halides.

The electrolyte composition of the present invention is molten at ambient temperatures over a wide composition range so as to provide basic (Al:Tim$<$1), neutral, (Al:Tim = 1) as well as

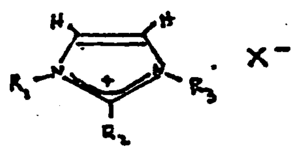
acidic (Al:Tim > 1) melts and shows improved electrochemical stability to oxidation and reduction compared to previously reported molten quaternary ammonium chloroaluminate melts. The electrolyte composition of the present invention may be used in a wide range of non-aqueous batteries including secondary batteries wherein at least one of the anode or cathode is a conjugated backbone polymer.

Accordingly, the present invention provides a molten, non-aqueous electrolyte composition comprising an admixture of aluminium halide, having the formula AlX_3 and 1,2,3-trialkylimidazolium halide, having the formula, TimX:



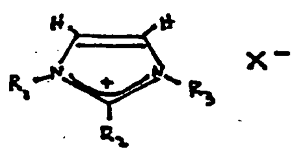
wherein R_1, R_2 and R_3 are independently alkyl of 1 to 12 carbons and wherein X is independently halide or mixtures of halides.

In a preferred embodiment of the present invention, there is provided a molten, non-aqueous electrolyte composition comprising an admixture of (a) aluminium halide having the formula AlX_3 and (b) 1,2,3-trialkylimidazolium halide having the formula TimX:



and (c) an electochemically inert organic liquid; wherein the molar ratio of Al to Tim is in the range of about 0.8:1 to about 2.0:1 and wherein R_1, R_2 and R_3 are alkyl groups of 1 to 12 carbons and X is independently halide or mixtures of halides.

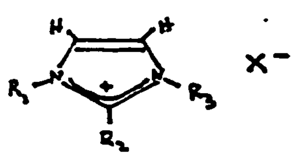
In another preferred embodiment of the present invention, there is provided a molten, non-aqueous electrolyte composition comprising an admixture of (a) aluminium halide having the formula AlX_3 and (b) 1,2,3-trialkylimidazolium halide having the formula, TimX:



an electrochemically inert organic liquid, wherein the molar ratio of Al to Tim is in the range of about 1.5:1 to about 2.5:1 and wherein R_1, R_2 and R_3 are independently alkyl of 1 to 12 carbons and wherein X is independently halide or mixtures of halides.

DETAILED DESCRIPTION OF THE INVENTION

The non-aqueous electrolyte compositions of the present invention are prepared by slow addition of an amount of aluminium halide, e.g., $AlCl_3$ or $AlBr_3$ to a known weight of 1,2,3-trialkylimidazolium halide having the formula TimX:



in the appropriate weight ratio to give the desired molar ratio of aluminium (denoted by Al) to 1,2,3-trialkylimidazolium (denoted by Tim). The molar ratio of aluminium to Tim in the electrolyte composition may be varied over a wide range from about 0.6:1 to about 2.5:1 including preferred ranges such as about 0.8:1 to about 2.0:1, about 1.5:1 to about 2.5:1 and about 1.5:1 to about 2.0:1. Conveniently, the aluminium halide is slowly added to the 1,2,3-trialkylimidazolium halide contained in a vessel cooled to at least about 0°C and preferably

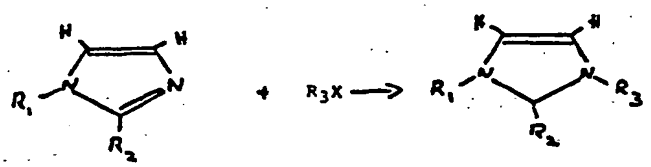
to about − 195° (b.p. of liquid N_2). The admixture so formed is thereafter heated, with stirring, at elevated temperatures in the range of about 50° − 100°C for several hours until a clear, slightly viscous ionic liquid is formed. The preparation and subsequent manipulation of the non-aqueous electrolyte compositions of the present invention are conveniently conducted under substantially water-free conditions and under an inert, substantially dry atmosphere, e.g., dry nitrogen or argon.

While water may be present during the preparation of electrolyte compositions of the present invention, water deleteriously affects the use of the electrolyte compositions in batteries and as such must be removed prior to use.

In addition to the admixture of aluminium halide and trialkylimidazolium halide of formula TimX, the electrolyte composition of the present invention may also contain an electrochemically-inert organic liquid and/or an alkali metal salt and/or tetraalkylammonium salt, e.g. $Li^+AlBr^-_4$ or $Bu_4N^+SbCl^-_6$ as hereinafter described.

The organic liquids which may be included in the electrolyte compositions of the present invention should be electrochemically inert to oxidation and reduction during use while simultaneously affecting a reduction in the viscosity and/or an improvement in the conductivity and stability of the electrolyte compositions of the present invention. Examples of such organic liquids include propylene carbonate, sulfolane, 3-methyl-2-oxazolidone, alkane sultones, e.g., propane sultone, butane sultone, (the use of sultones in electrolyte compositions is the subject of USSN 556717) and the use of sultones for coatings on polymer anodes is the subject of EPC Application 84112703.8) dimethyl sulfoxide (DMSO), dimethyl sulfite, cyclic ethers, e.g. tetrahydrofuran (THF), 2-methyltetrahydrofuran (2-MeTHF), glymes, alkanoyl and aranoyl nitriles, e.g. acetonitrile, proprionitrile, butyronitrile and benzonitrile, dichloromethane, tetraethylsulfamide, aromatic hydrocarbons, e.g. toluene and benzene, and nitrobenzene. The organic liquid chosen will, of course, depend upon many factors, such as the precise electrolyte composition used, the voltage range desired, the anode and cathode used as well as other components of the battery.

The 1,2,3,-tri(C_1−C_{12})alkylimidazolium halide, TimX, contained in the electrolyte composition of the present invention is conveniently prepared by reaction of a 1,2,-di(C_1−C_{12}) alkylimidazole with at least a stoichiometric amount of a (C_1−C_{12})alkyl halide, R_3X, as shown in the following scheme:



TimX

The halide, X, may independently be fluoride, iodide, bromide or chloride or mixtures of halides, preferably iodide, bromide or chloride, but bromide and chloride are more preferred. The R_1, R_2 and R_3 groups are linear and branched alkyl of 1 to 12 carbons. Particularly suitable alky groups include linear alkyl groups such as methyl, ethyl, n-propyl, n-butyl and n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl and n-dodecyl. For those alkyl groups having more than 5 carbons, branched alkyl groups such as i-hexyl or i-octyl may also be used. While R_1 to R_3 may be the same, e.g., n-butyl, particularly useful electrolyte compositions were prepared wherein R_1 and R_2 were methyl and R_3 was ethyl or n-propyl or n-butyl. Since it is believed that conductivity of the electrolyte compositions of the present invention should vary inversely with the size and number of carbon atoms in R_1, R_2 and R_3, it is preferred that R_1, R_2 and R_3 independently be linear alkyl containing 1 to 5 carbons.

In a preferred preparative scheme, the 1,2-dimethyl-3-ethylimidazolium chloride and the corresponding bromide were prepared by reaction of 1,2-dimethylimidazole (R_1 and R_2 were methyl) with a large excess (four-fold volume excess) of chloroethane (R_3X was C_2H_5Cl) and bromoethane, (R_3X was C_2H_5Br), respectively.

The reaction was conveniently conducted in a pressure vessel. The reaction mixture of dialkylimidazole and alkyl halide was heated at elevated temperature, e.g., 70°C, with stirring, for several days. The pressure was thereafter released and the excess alkyl halide was removed with mild heat. The crude product was recrystallized (to constant melting point) under an inert atmosphere. The resulting 1,2,3-trialkylimidazolium halide, TimX, was then admixed with aluminium halide as previously described.

The electrolyte composition of the present invention may be used in a variety of non-aqueous primary and secondary batteries.

While the major components of such batteries include electrodes (anode and cathode), the electrolyte composition of the present invention (additionally containing a suitable electrochemi-

cally-inert organic liquid and/or an alkali metal or salt and/or tetraalkylammonium salt), and conventional or unconventional housing, charging mechanism, current collector and the like, only the electrodes and electrolyte composition will be described.

Numerous combinations of anodes and cathodes may be used with the electrolyte composition of the present invention. In one such combination, the anode may comprise alkali metal alloys or amalgams such as lithium-aluminium alloys (but alkali metals in the zero valence state, e.g., lithium are to be avoided), or lithiated transition metal chalcogenides such as Li_xWO_2, Li_yVSe_2, Li_yVS_2, Li_yTiS_2 or Li_yMoO_2 ($0<x\leq1$, $1<y\leq2$) into which alkali metal cations (especially Li^+) are inserted during charging and the cathode may comprise a transition metal chalcogenide (such as TiS_2, MoS_3, V_6O_{13} or Li_xCoO_2) into which alkali metal cations (especially Li^+) are inserted during discharging. Suitable such transition-metal chalcogenides are listed on page 392 of "Lithium Batteries" (J.P. Gabano, ed., 1983) with those having average voltages as cathodes of 2.3V or greater being preferred, including V_6O_{13}, $Cr_yV_{1-y}S_2$ ($0.25\leq y\leq0.75$), Cr_3O_8, Li_xCoO_2 ($0<x\leq1$) and MoO_3 and the cathode may be transition-metal halides or oxyhalides insoluble under certain conditions such as iron(III)chloride, cobalt(III)chloride, iron(III)oxychloride, or chromium(III)oxychloride..

In a second such combination, which, in addition to the first such combination hereinabove, are the subject of USSN 556497, the anode comprises aluminium and the cathode comprises a member selected from the group consisting of graphite, iron sulfides on a carbon support, intercalation compounds of graphite, transition-metal chalcogenides, transition-metal halides, transition-metal oxyhalides, and conjugated backbone polymers.

Suitable intercalation compounds of graphite are described by M. Armand and P. Touzain in *Mater; Sci. and Eng.*, Vol. 31, pages 319–329 (1977). Such intercalation compounds include transition metal chlorides, bromides, and fluorides which are, e.g. $AlBr_3$, BF_3, $FeCl_3$, $FeBr_3$, TiF_4, $CoCl_2$, $HgCl_2$, $SbCl_5$, $MoCl_5$, $AlCl_3$, WCl_6, $NiCl_2$ and $CrCl_3$.

The transition metal chalcogenides suitable as cathodes are the same as those described in reference to the cathodes for the first combination hereinabove.

Conjugated backbone polymers suitable as cathodes are those polymers which are capable of being oxidized (acceptor-doped).

In their most heavily oxidized state such polymer cathode materials range in voltage from about 3.0V to about 4.6V vs Li/Li^+ (for measurement made in various typical organic electrolytes). In ascending order of approximate voltage vs Li/Li^+, examples of such polymers useful as cathode materials include oxidized polypyrrole (PP), polyacetylene (PA), polyaniline, polyazulene (PAZ), polythiophene (PT), poly(phenylene vinylene) (PPV), polyacenediyls (e.g. polynaphthalenediyl (PN)), polyacenes, poly(p-phenylene) (PPP), polythianthrene (PTA), poly(phenothiazine) (PPT), poly(phenylene sulfide) (PPS), and poly(phenylene oxide) (PPO).

Also included are substituted versions of the above or copolymers of the above or other polymers having conjugation along at least one backbone thereof and rendered conductive by electrochemical doping with either cations, anions, or both.

For such a second combination wherein the anode comprises an aluminium anode, the useful electrolyte composition of the present invention comprises an admixture of aluminium halide, e.g., $AlCl_3$, and a 1,2,3-trialkylimidazolium halide of formula TimX wherein the molar ratio of Al:Tim is greater than about 1:1 to about 2.5:1 so that the molten electrolyte composition is an acidic melt, i.e., Al:Tim>1:1, e.g., about 1.5:1 to 2.5:1, preferably about 1.5:1 to 2.0:1. When a conjugated backbone polymer is chosen as the cathode material, anions of the molten electrolyte compositions of the present invention will be inserted into the polymer during the charging of the battery. In the acid melt described herein, the anions inserted will likely be of the form $AlCl_3X^-$ or $Al_2Cl_6X^-$ wherein X is independently halide which may be fluoride, bromide, chloride or iodide, preferably chloride, bromide or iodide but more preferably chloride or bromide. Additional salts, alkali-metal (e.g., Li^+, Na^+, K^+) or tetraalkylammonium (e.g., Me_4N^+, Et_4N^+ or η-Bu_4N^+) may also be incorporated into the molten electrolyte composition of the present invention and the anion of such salts is typically halide, e.g., I^-, Cl^- or Br^- or AlX_4^-, e.g., $AlCl_4^-$, $AlBr_4^-$ or $AlCl_3Br^-$ but may also be, for example, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, BCl_4^-, PCl_6^- PCl_4^-, $MoCl_6^-$, $SbCl_4^-$, $SbCl_6^-$, $AsCl_6^-$ or $FeCl_4^-$ and corresponding bromides or mixtures of halides.

It is to be understood that addition of a particular Lewis Acid salt may be accomplished either by addition of the Lewis Acid salt itself (e.g., $Li^+AlBr_4^-$, $Li^+FeCl_4^-$ or $Li^+SbCl_6^-$) or by addition of the corresponding alkali metal or tetraalkylammonium halide (a Lewis Base in these melts) plus a Lewis Acid, i.e., e.g., $LiBr + AlBr_3$, $LiCl + FeCl_3$ or $LiCl + SbCl_5$). The proportions of added Lewis Base Acid need not always be equal, and is some instances only a Lewis Base e.g., Li^+Cl^- or $Me_4N^+Cl^-$ or Lewis Acid (e.g., $SbCl_5$) may be added.

In the third and fourth combinations wherein the anode is a conjugated backbone polymer capable of being reduced (donor-doped), such as polyacetylene, the electrolyte composition of the present invention preferably may further comprise an alkali metal (Li^+, Na^+, K^+) and/or tetraalkylammonium salt. The anion of such a salt may be any anion that is non-reactive (non-

oxidizing or non-reducing) in use such as halides such as I^-, Br^-, or Cl^-, or AlX_4^-, e.g., $AlBr_4^-$, $AlCl_3Br^-$ or $AlCl_4^-$, but also may be BF_4^-, PF_6^-, PCl_6^-, PCl_4^-, $FeCl_4^-$, ClO_4^-, $SbCl_4^-$, $MoCl_6^-$, SbF_6^-, $SbCl_6^-$, AsF_6^-, $AsCl_6^-$ or BCl_4^- and corresponding bromides or mixtures of halides.

In the third and fourth such combinations, which are the subject of a separate, commonly assigned U.S. Patent Application of Gifford, Shacklette, Toth and Wolf (Attorney's Docket No. PD 82-2190C) and filed on an even date herewith and hereby incorporated by reference, the anode and cathode independently comprise a conjugated backbone polymer selected from those described hereinabove and/or transition-metal chalcogenides, also selected from those described hereinabove. In such a third combination the useful electrolyte composition of the present invention may comprise an essentially equimolar admixture of aluminium halide, AlX_3, and 1,2,3-trialkylimidazolium halide of formula TimX, but also comprise a molten electrolyte composition wherein the molar ratio of Al (in aluminium halide) to Tim (in TimX) is less than about 1 : 1. In such event the anode is a conjugated backbone polymer into which cations (especially alkali metal or tetraalkylammonium cations) are electrochemically inserted during charging. The cathode may either be inserted by cations during discharging or by anions (especially the anion of the salt as tetrafluoroborate, perchlorate, hexafluoroarsenate, hexafluorophosphate or tetrachloroaluminate) during charging.

In the fourth combination, the anode is such a conjugated backbone polymer into which cations (especially alkali metal cations) are inserted during charging and the cathode is a transition metal chalcogenide (such as TiS_2, MoO_3, V_6O_{13} or Ki_xCoO_2 wherein $0<x\leq1$) into which alkali metal cations (especially Li^+) are inserted during discharging. Suitable such transition metal chalcogenides are exactly those described hereinabove in the second combination wherein the anode comprises aluminium.

Examples 1–6 and 9–11 illustrate the present invention. Examples 7 and 8 illustrate the utility of the electrolyte composition of the present invention in a secondary battery and is a related invention of commonly-assigned U.S. Patent application of Gifford, Palmisano, Shacklette, Chance and Toth (Attorney's Docket # 82-2190B).

Example 1. *Preparation of 1,2-dimethyl-3-ethylimidazolium bromide.* The salt 1,2-dimethyl-3-ethylimidazolium bromide was prepared by refluxing 21 mL of 1,2-dimethylimidazole (Aldrich Chemical Co.) with a four-fold mole excess of bromoethane, 60 mL (Aldridge Chemical Co.) in a clean dry 250 mL flask. The 1,2-dimethylimidazole had been previously purified by vacuum distillation.

This mixture was allowed to reflux for two days. The excess bromoethane was distilled off and the crude salt dried under vacuum to remove the last traces of bromoethane.

The crude product, an off-white powder, was recrystallized from acetonitrile/ethyl acetate under a dry inert atmosphere, followed by vacuum drying to give a white crystalline solid. The structure of the product was verified by NMR spectroscopy.

Example 2. *Preparation of 1,2-dimethyl-3-ethylimidazolium chloride.* The salt 1,2-dimethyl-3-ethylimidazolium chloride was prepared by reacting 14 mL of 1,2-dimethylimidazole with 56 mL of chloroethane (Eastman Kodak) under a pressure of 40 psig. A measured volume (14 mL) of distilled 1,2-dimethylimidazole was placed in a 200 mL pressure reaction vessel in a dry, inert atmosphere of argon. Chloroethane was vacuum distilled into the pressure vessel to give an approximately four-fold volume excess.

This mixture was heated to approximately 70°C with stirring. Reaction was allowed to proceed for four days at which time the excess chloroethane was removed by vacuum distillation followed by drying under vacuum to yield an off-white solid. This material was recrystallized from acetonitrile/ethyl acetate under a dry, inert atmosphere, followed by vacuum drying to give a white, crystalline solid. The structure of the product was verified by NMR spectroscopy.

Example 3. *Preparation of 1,2-dimethyl-3-butylimidazolium chlorides.* The salts 1,2-dimethyl-3-propylimidazolium chloride and 1,2-dimethyl-3-butylimidazolium chloride were prepared in accordance with the procedure of Example 2 except that chloroethane is replaced by 1-chloropropane (Aldrich Chemical Co.) and 1-chlorobutane (Aldrich Chemical Co.), respectively.

Example 4. *Preparation of a 2 : 1 (mole/mole) admixture of $AlCl_3$: 1,2-dimethyl-3-ethylimidazolium chloride.* A molten salt electrolyte was prepared by slow addition of 15.6 g of $AlCl_3$ (Fluka Chemical Corp.) to 12 g of 1,2-dimethyl-3-ethylimidazolium chloride. The receiving flask was cooled with liquid nitrogen to −195°C and the $AlCl_3$ added gradually, in portions, under a dry, inert argon atmosphere. The salt mixture was periodically allowed to warm to room temperature and then cooled prior to addition of $AlCl_3$.

After all the $AlCl_3$ had been added, the salt mixture was gradually heated to approximately 50°C with stirring to give a clear liquid of a slight orange-brown color. This liquid was

preelectrolyzed at a constant current of 100 mA using two aluminium electrodes to give a clear, nearly colorless liquid.

The conductivity of this electrolyte was measured using a glass conductivity cell and an impedance bridge. A value of 7.1 mS cm^{-1} was obtained at 25°C for this electrolyte.

Example 5. *Neutral melt of LiCl 2:1 (mole/mole) $AlCl_3$: 1,2-dimethyl-3-ethylimidazolium chloride.* A 2:1 (mole/mole) $AlCl_3$: 1,2-dimethyl 1-3-ethylimidazolium chloride melt was prepared as described in Example 4. The salt, LiCl (approx. 400 mg) was gradually added to 10 g of this melt until a neutral composition, as defined by the following formula: (moles of $AlCl_3$ = (moles of Im^+ + moles of Li +) was obtained. The neutrality of this melt was confirmed by cyclic voltammetry as indicated by the absence of a peak for $Al_2Cl_7^-$ reduction and further confirmed by infrared spectroscopy which showed strong absorption bands for $AlCl_4^-$ and no bands for $Al_2Cl_7^-$. This electrolyte was liquid at room temperature.

Example 6. *Addition of benzene to a 2:1 (mole/mole) $AlCl_3$: TimCl Electrolyte* A 2:1 (mole/mole) $AlCl_3$: 1,2,-dimethyl-3-ethylimidazolium chloride melt was prepared as described in Example 4. Dry benzene (5 mL) was added to give a 50:50 volume percent solution. The benzene was totally miscible with the melt at this concentration to give a clear, slightly gold colored liquid of lower viscosity which should lead to higher conductivity than that of the pure melt.

Example 7. *Recyclability of Al Electrode* A cell containing the electrolyte, 2:1 (mole/mole) admixture of $AlCl_3$: 1,2-dimethyl-3-ethylimidazolium chloride prepared in accordance with the procedure of Example 4, a tungsten working electrode (Alfa Products) and an aluminium foil electrode (Alfa Products) was assembled. Al was successfully electrodeposited onto the W foil at a current density of 0.5 mA cm^{-2} to give a granular, matte deposit. The as-plated Al was successfully stripped and replated for 40 cycles at >90% coulombic efficiency. This Example demonstrates (1) that aluminium is plated onto a tungsten electrode using the electrolyte composition of the present invention and (2) that aluminium can be successfully electrochemically cycled and (3) that the electrolyte of the present invention would be useful in secondary battery applications using an aluminium negative electrode.

Example 8. *Al/Graphite Battery* A battery was constructed consisting of an Al negative electrode (Johnson Matthey Chemicals Ltd.) and a graphite positive electrode (Alfa Products) submerged in the electrolyte prepared as described in Example 4. The cell showed an open circuit voltage of 1.7V. This cell was successfully repeatedly charged and discharged at a charging current of 1mA followed by discharging at 0.5 mA for one hour. During charging the cell voltage rose to 2.0V. On discharge an average cell voltage of 1.6V was observed. This Example illustrates, that the electrolyte composition of the present invention is useful in a secondary battery having an aluminium anode.

Example 9. *Phase Diagram for $AlCl_3$: 1,2-dimethyl-3-ethylimidazolium bromide molten salt system.* The liquid-to-solid transition temperature was determined for the $AlCl_3$: 1,2-dimethyl-3-ethyl-imidazolium bromide system over the range of 0.2 of 0.8 mole fraction of $AlCl_3$ where mole fraction is defined as (moles AlX_3)/(moles AlX_3 + moles TimX). Weighed portions of $AlCl_3$ were added to 1,2-dimethyl-3-3ethylimidazolium bromide salt of Example 1, heated until liquid and allowed to cool gradually. The liquid-to-solid transition was visually determined and the temperature monitored with a glass-encased thermocouple. These temperatures were plotted versus mole fraction.

The phase diagram has two minima; one at 0.42 mole fraction and a second at 0.67 mole fraction. The freezing point at 0.67 mole fraction $AlCl_3$ occurs at about −25°C and is most likely a glass transition temperature. This point was obtained by cooling a sample of the melt in dry ice-acetone and observing the liquid transition temperature during warming.

The diagram shows a maxima at 0.5 mole fraction with a freezing point of 80°C. The system is molten at room temperature (≤25°C) only about a narrow range of 0.64 to 0.72 mole fraction $AlCl_3$. It is expected that the phase diagram for $AlCl_3$:TimCl would not differ significantly. However the case of preparing a neutral melt by addition of LiCl as described in Example 5 gave an electrolyte that was liquid at 20°C.

Example 10. *Preparation of a 1:1 (mole/mole) admixture of $AlCl_3$: 1,2-dimethyl-3-propylimidazolium chloride.*

A molten salt electrolyte was prepared by slow addition of 2.3 g $AlCl_3$ (Fluka Chemical Corp.) to 3.0 g of 1,2-dimethyl-3-propylimidazolium chloride in an analogous fashion as that stated in Example 4. Following addition of the $AlCl_3$, an orange-colored liquid which was molten at 20°C was obtained. This Example illustrates that higher substituted imidazolium salts (i.e., 3-propyl

compared to the 3-ethyl substituted imidazolium of Example 9) should provide electrolytes that are molten or liquid over a wider composition range, i.e. wider molar ratio of $AlCl_3$:TimX.

Example 11. *Reduction Potentials of Quaternary Ammonium Salts* The reduction potentials of a series of quaternary ammonium compounds were measured in acetonitrile, tetramethylammonium perchlorate (Fluka Chemical Corp.) electrolyte. Reduction potentials were measured from the peak current response obtained at a Pt disk working electrode (Bioanalytical Systems) versus a silver wire reference electrode (Alfa Products). Values are listed in Table I and illustrate the increased stability of the trialkylimidazolium cation to electrochemical reduction compared to previously known molten salt systems.

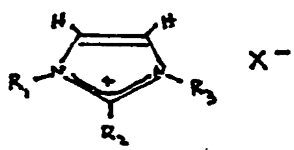
Table I

Compound	E_{red} *(volts Vs Ag)*
N-Butylpyridinium chloride	− 1.10
1-methyl-3-ethylimidazolium bromide	− 1.70
1,2-dimethyl-3-ethylimidazolium bromide	− 2.20

Similar results would be expected for the reduction potentials obtained on the above-listed quaternary ammonium halides in combination with amounts of AlX_3, e.g., $AlCl_3$, so as to form neutral or basic melts.

CLAIMS

1. A molten, non-aqueous electrolyte composition comprising a mixture of an aluminium halide, having the formula AlX_3 and 1,2,3-trialkylimidazolium halide, having the formula TimX:



(Tim X)

wherein R_1, R_2 and R_3 are independently alkyl of 1 to 12 carbons and wherein X is independently halide or a mixture of halides.

2. An electrolyte composition according to claim 1 wherein the molar ratio of aluminium to 1,2,3-trialkylimidazolium is from 0.6:1 to 2.5:1.

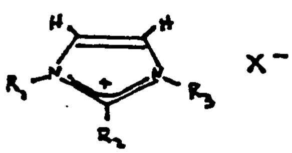
3. An electrolyte composition according to claim 1 or 2 wherein R_1, R_2 and R_3 are linear alkyl groups of 1 to 5 carbons.

4. An electrolyte composition according to claim 3 wherein R_1 and R_2 are methyl and wherein R_3 is ethyl, n-propyl or n-butyl.

5. An electrolyte according to any one of the preceding claims which further comprises an electrochemically-inert organic liquid.

6. An electrolyte according to any one of the preceding claims which further comprises an alkali metal or tetraalkylammonium salt or a mixture thereof.

7. A molten, non-aqueous electrolyte composition comprising a mixture of (a) an aluminium halide having the formula AlX_3 and (b) a 1,2,3-trialkylimidazolium halide having the formula



(Tim X)

and (c) an electrochemically-inert organic liquid; wherein the molar ratio of Al to Tim is from 0.8:1 to 2.5:1 and wherein R_1 to R_3 are independently alkyl of 1 to 12 carbons and wherein X is independently halide or a mixture of halides.

8. An electrolyte according to claim 7 which further comprises an alkali metal or tetraalkylammonium salt or mixture thereof.

9. An electrolyte according to any one of the preceding claims wherein X is chloride or bromide in AlX_3 and in TimX.

10. An electrolyte according to any one of the preceding claims wherein the molar ratio of Al to Tim is from 1.5:1 to 2.0:1.

11. An electrolyte composition according to claim 1 substantially as described with reference

to any one of Examples 4 to 6 and 10.

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